

**We claim:**

1. A method for rendering a porous substrate repellent to water and/or oil-based stains comprising;

5        1) applying to the substrate an aqueous composition comprising polymers having interpolymerized units derived from one or more of each of the following monomers:

10            (a) monomer selected from the group consisting of acrylate, methacrylate, acrylamide, methacrylamide, thioacrylate and meththioacrylate compounds containing a fluoroaliphatic moiety that is linked to the residue of the

compound through a divalent, organic linking group;

15            (b) monomer selected from the group consisting of acrylic acid, methacrylic acid, carboxyalkylacrylate and carboxyalkylmethacrylate compounds;

                  (c) monomer selected from the group consisting of acrylate, methacrylate, acrylamide, methacrylamide, thioacrylate and meththioacrylate compounds containing an alkoxysilane moiety linked to the residue of the compound through a divalent organic group; and

                  (d) optionally other monomers containing a non-hydrophilic group; and

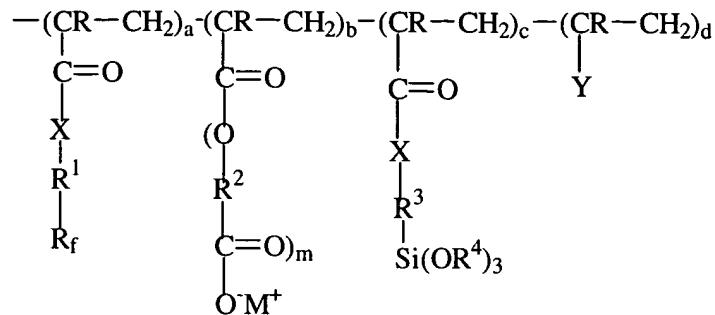
20        2) allowing the composition to penetrate the surface of the article, and allowing the composition to cure on the substrate surface.

2. The method of claim 1 wherein the substrate is cured at ambient temperatures.

25        3. The method of claim 1 wherein said substrate is selected from the group consisting of masonry, concrete, asphalt, wellbores, textiles, carpets, plastics, painted surfaces, and leathers.

30        4. The method of claim 1 wherein said polymer has a number average molecular weight between about 3500 and about 100,000 and a molecular weight distribution of greater than 1.5.

5. The method of claim 1, said polymers having the formula:



5 wherein:

R is hydrogen or an aliphatic group having from 1 to 4 carbon atoms;

R<sub>f</sub> is a fluoroaliphatic group having a carbon chain from 3 to 6 carbon atoms in length;

R<sup>1</sup> is an organic divalent connecting group;

10 X is independently selected from the group consisting of oxygen, nitrogen, or sulfur;

R<sup>2</sup> is a short chain alkylene group;

m is 0 or 1;

M<sup>+</sup> is hydrogen atom or a mono- or multivalent cation;

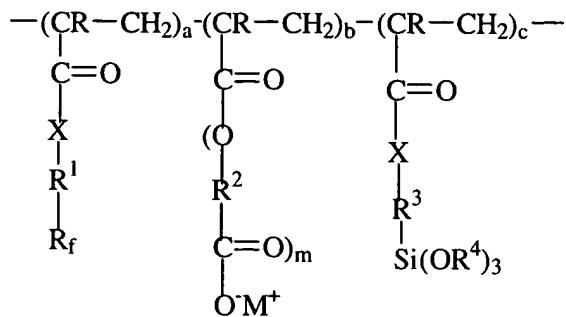
15 R<sup>3</sup> is an organic divalent connecting group;

R<sup>4</sup> is hydrogen, or a methyl, ethyl, or butyl group;

Y is a non-hydrophilic group and

a, b, c are ≥ 1 and d ≥ 0 .

20 6. The method of claim 1, said polymers having the formula:



wherein:

R is hydrogen or an aliphatic group having from 1 to 4 carbon atoms;

5 R<sub>f</sub> is a fluoroaliphatic group having a carbon chain from 3 to 6 carbon atoms in length;

R<sup>1</sup> is an organic divalent connecting group;

X is independently selected from the group consisting of oxygen, nitrogen, or sulfur;

10 R<sup>2</sup> is a short chain alkylene group;

m is 0 or 1;

M<sup>+</sup> is hydrogen atom or a mono- or multivalent cation;

R<sup>3</sup> is an organic divalent connecting group;

R<sup>4</sup> is hydrogen, or a methyl, ethyl, or butyl group; and

15 a, b, and c are ≥ 1.

7. The method of claim 6 wherein:

R<sup>1</sup> is selected from the group consisting of —C<sub>y</sub>H<sub>2y</sub>—,

—CON(R<sup>5</sup>)C<sub>y</sub>H<sub>2y</sub>—, —SO<sub>2</sub>N(R<sup>5</sup>)C<sub>y</sub>H<sub>2y</sub>—, and —C<sub>y</sub>H<sub>2y</sub>SO<sub>2</sub>N(R<sup>5</sup>)C<sub>y</sub>H<sub>2y</sub>—,

20 where R<sup>5</sup> is hydrogen, or a methyl, ethyl, propyl, or butyl group and y is

independently selected as between 1 and 6 inclusive; and

R<sup>2</sup> and R<sup>3</sup> are each independently is a methylene, ethylene, propylene, or butylene group.

8. The composition of claim 1 wherein said polymer has a number average molecular weight between about 10,000 and about 75,000 and a molecular weight distribution of greater than 2.

5 9. The method of claim 1, wherein said polymers contain only carbon atoms in the backbone of the polymer chain, consisting essentially of interpolymerized units of (a) 40 to 80 weight percent of monomers containing fluoroaliphatic groups, (b) 5 to 50 weight percent of monomers containing carboxyl groups, (c) 1 to 20 weight percent of monomers containing silyl groups and (d) 0 to 20 weight percent of other monomers having a non-  
10 hydrophilic group.

10. The method of claim 1, wherein said polymers contain only carbon atoms in the backbone of the polymer chain, consisting essentially of interpolymerized units of (a) 50 to 75 weight percent of monomers containing fluoroaliphatic groups, (b) 5 to 25 weight  
15 percent of monomers containing carboxyl groups, (c) 2 to 15 weight percent of monomers containing silyl groups and (d) 0 to 5 weight percent of other monomers having a non-  
hydrophilic group.

11. The method of claim 6, wherein said R<sub>f</sub> group is perfluorinated.

20 12. The method of claim 1 wherein said monomers (d) are selected from (meth)acrylate esters and amides, vinyl ethers, vinyl esters, and styrenes.

13. The method of claim 1 wherein said monomers a) are selected from the group  
25 consisting of C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>N(CH<sub>3</sub>)C<sub>2</sub>H<sub>4</sub>OC(O)CH=CH<sub>2</sub>;  
C<sub>5</sub>F<sub>11</sub>SO<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)C<sub>2</sub>H<sub>4</sub>OC(O)CH=CH<sub>2</sub>;  
C<sub>6</sub>F<sub>13</sub>SO<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)C<sub>2</sub>H<sub>4</sub>OC(O)C(CH<sub>3</sub>)=CH<sub>2</sub>;  
C<sub>3</sub>F<sub>7</sub>SO<sub>2</sub>N(C<sub>4</sub>H<sub>9</sub>)C<sub>2</sub>H<sub>4</sub>OC(O)CH=CH<sub>2</sub>; C<sub>4</sub>F<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>;  
C<sub>5</sub>F<sub>11</sub>CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>; C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>, and  
30 the reaction product of one mole each of C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)C<sub>2</sub>H<sub>4</sub>OH,  
HOC<sub>3</sub>H<sub>6</sub>OC(O)C(CH<sub>3</sub>)=CH<sub>2</sub> and toluene diisocyanate.

14. The method of claim 1 wherein said monomers (b) are selected from the group consisting of acrylic acid, methacrylic acid and carboxyethylacrylate.

5 15. The method of claim 1 wherein said monomers (c) are selected from the group consisting of 3-acryloxypropyl trimethoxysilane, 3-methacryloxypropyl trimethoxysilane, and vinyltriethoxysilane.

16. A porous substrate treated with the method of claim 1.